

## DIFFERENTIAL SCANNING CALORIMETRY OF PHYLLOSILICATE MINERALS AT REDUCED PRESSURES: A MINERAL DATABASE FOR THE THERMAL EVOLVED GAS ANALYZER (TEGA).

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**Introduction:** As a result of experimental data acquired from Mars thus far (e.g., Viking GC-MS data, orbital reflectance spectral data), there are indications that phyllosilicate minerals may exist among the volatile bearing materials found in the regolith. The confirmation (or refutation) of certain mineral phases would provide insight into the past climate of Mars and whether liquid water existed on the surface in substantial quantities. The failed Mars '98 Lander carried an instrument -Thermal Evolved Gas Analyzer (TEGA)- that would have been used to characterize these minerals. Plans are to re-optimize TEGA in anticipation that the instrument will fly again on upcoming Mars landers. TEGA is made up of a series of single-slot furnaces, which will heat the collected surface materials under a slow stream of N<sub>2</sub> (0.4 sccm\*) at near 100 Torr. Differences in power consumption between sample and reference furnaces will be recorded as a function of the temperature, and evolved gases will be analyzed. Experiments are currently being conducted on a TEGA-like laboratory instrument at NASA Johnson Space Center, which employs a differential scanning calorimeter (DSC) hooked up to a quadrupole mass spectrometer (QMS). In previous experiments using different groups of minerals it was found that the flow rate and pressure of the carrier gas would influence the onset temperature and enthalpies of these minerals [1]. This being the case, in order to evaluate the data taken on Mars from a TEGA-like instrument, it is necessary to have a database of enthalpy and onset temperature "signatures" for a variety of volatile bearing materials at reduced pressures and gas flow rates [2]. This paper will focus specifically on phyllosilicates.

We have chosen two source clay minerals from the American Clay Minerals Society to test; kaolinite (KGa-1), (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), which is a 1:1 layered phyllosilicate, and nontronite (SWa-1), (Na<sub>0.33</sub>Fe<sup>3+</sup><sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub> · n(H<sub>2</sub>O)), which is a 2:1 expandable layered phyllosilicate. Kaolinite was chosen because it has one very distinct dehydroxylation DSC peak. Kaolinite is closely associated with regions of hydrothermal alteration, and may provide evidence if such an environment was once present on Mars. Nontronite was chosen because it has a 2:1 phyllosilicate and it

has two distinct DSC endothermic peaks due to evolution of interlayer water and structural dehydroxylation. Nontronite has been suggested as a possible candidate for the O<sub>2</sub> release from the gas exchange experiment on Viking [3]. The objective of this paper was to focus on the thermal behaviors of these two phyllosilicates under reduced pressure conditions.

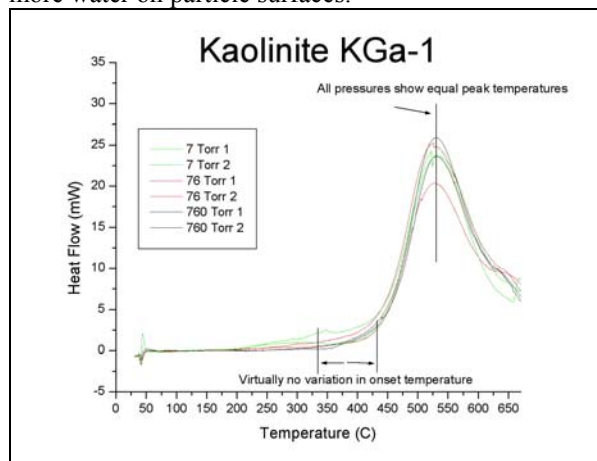
**Materials and Methods:** A Perkin Elmer DSC-7 apparatus was modified in order to vary the pressure on the test samples. An electronic mass flow meter and a serial vacuum pump, in conjunction with needle valves for flow control, were part of the modifications made to control the gas flow and pressure within the oven chamber. The carrier gas flow rate was fixed to 28.4 sccm of Ar gas. The QMS accepts flow at a maximum intake pressure of 14 sccm for 760 and 76 Torr pressures and 2.5 sccm for 7 Torr pressures, with the remaining gas bypassed. Sample weights introduced into the DSC ovens were also kept fairly consistent at ~5.5 mg in order to minimize differences in the interaction between the carrier gas and the sample's particle packing density. The samples were heated in a platinum oven with a temperature ramp rate of 20°C/min. At each pressure (7, 76, 760 Torr), two separate runs were conducted to make sure results were repeatable.

**Results and Discussion:** The DSC signatures for kaolinite at the three varied pressures can be seen in the curves of Figure 1 with the accompanying data in Table 1. Pressure does not seem to have much effect on the dehydroxylation of kaolinite. The temperature at the peak of dehydroxylation occurred at ~530°C, with the onset temperature for all three pressures nearly the same at ~445°C. The enthalpies were also calculated for each test, although by the very rough means of calculating the approximate area under the curve. There is enough fluctuation, depending upon the small differences in the sample and its packing, that enthalpy is not a very useful measurement here.

The DSC curves for nontronite are shown in Figure 2, with the data in Table 1. Unlike kaolinite, nontronite has two endothermic peaks, the first at 100°C is due to the loss of H<sub>2</sub>O associated with the interlayer cation (Na in this case), and the second due to structural dehydroxylation had peak temperatures between 460 and 400° C, depending upon pressure. Further-

\* Standard cubic centimeters per minute

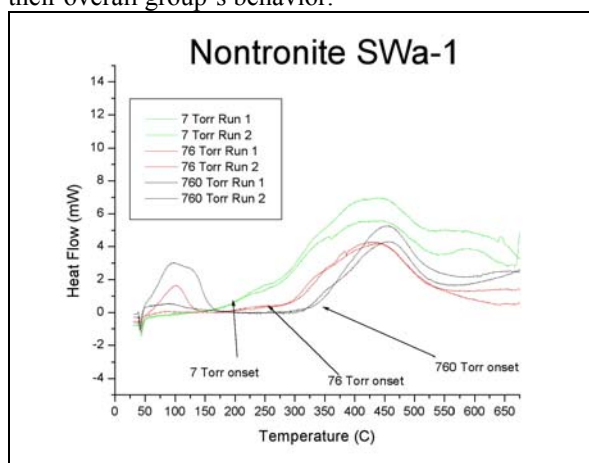
more two different grain sizes of nontronite were used to show the dependence of thermal signature on material properties. The first run at each pressure used a fine powdery sample ( $<0.2 \mu\text{m}$ ) while the second run used a coarse flaky material ( $<2 \mu\text{m}$ ). Comparing the first endothermic reaction (peak temperature of  $100^\circ\text{C}$ ) of the two it can be seen that, more water is lost from the fine-grained nontronite than the larger particle-sized sample. This is in line with expectations as the smaller particles have a larger surface area and absorb more water on particle surfaces.



**Figure 1-** Reduced Pressure DSC curves of kaolinite

The shifting of the peak and onset to lower temperatures, with a decrease in pressure for the second endotherm of nontronite, is what was expected prior to testing. The same however was expected of kaolinite but was not observed. What then is the difference between the two minerals that could be the possible reason for this? The differences between the two is that kaolinite is a 1:1 phyllosilicate with an Al-OH bond involved during dehydroxylation, whereas nontronite is a 2:1 phyllosilicate with a Fe-OH bond. It is possible that bond energies, i.e., higher bond energy for Al-OH than Fe-OH may be responsible for the lower temperatures observed for onset temperature at reduced pressures, although this requires further studies. Previous research has shown that the same kao-

linite at pressures greater than 760 Torr starts to show an increase in onset temperature[4]. This is consistent with the assertion that higher pressure serves to further stabilize the internal structure and bonds. The reason no noticeable effects are seen with decreasing pressure could indicate a stable structure in kaolinite, which is not susceptible to bond weakening at lower pressures. The same study did show however that at high enough pressures the trend reverses and the peak again shifts toward lower onset temperatures. Most 2:1 phyllosilicates, however, are more “elastic” in their bonds (i.e., lower bond energies). Future studies will seek to acquire reduced pressure curves for other phyllosilicates as well as investigate the differences between bonds in 1:1 and 2:1 phyllosilicates in more detail, to see if the results of kaolinite and nontronite are representative of their overall group’s behavior.



**Figure 2-** Reduced Pressure DSC curves of nontronite

**References:** [1] Lauer, H. V., et. al., *Lunar and Planetary Science XXIX*, CD\_ROM. [2] Golden, D.C., et. al. 1998 *Agronomy Abstracts*, SSSA, Madison, WI. [3] Banin, A., et. al, *Surface Chemistry and Mineralogy*, in Keiffer, et. al, *Mars*, pp. 595-625. [4] Yeskis, D., et. al., *American Mineralogist*, Volume 70, pp. 159-164.

**Table 1-** Thermal Analysis Data for Kaolinite and Nontronite at Reduced Pressures

Sample	Sample Weight Before(mg)	Sample Weight After(mg)	Pressure (Torr)	DSC Gas Flow Rate (sccm)	Enthalpy 1 (J/g)	Onset Temp 1	Temp @ Enthalpy Peak 1 (°C)	Enthalpy 2 (J/g)	Onset Temp 2	Temp @ Enthalpy Peak 2 (°C)
Kaolinite (Kga-1*)	5.49	N/A	760	20	~1600	~456	530.6			
	5.19	N/A	760	20	~1500	~435	532.5			
	5.11	4.39	76	20	~1000	~440	529.2			
	5.51	4.69	76	20	~1300	~452	530.6			
	5.6	4.74	7	20	~1100	~455	522.2			
	5.83	4.93	7	20	~980	~450	530.6			
Nontronite (SWA-1*)	5.72	4.62	760	20	~130	~45	99.4	~250	~340	458.3
	5.14	4.43	760	20	~45	~43	99.4	~240	~310	459.2
	5.43	4.35	76	20	~30	~43	102.7	~300	~240	423.7
	5.16	4.57	76	20	~3	~50	100.3	~270	~230	433.5
	5.53	4.7	7	20	-	-	-	~350	~170	432.1
	5.09	4.26	7	20	-	-	-	~330	~170	442.4